EXPLORATORY TECHNOLOGY RESEARCH IN SUPPORT OF THE U.S. DEPARTMENT OF ENERGY ELECTRIC AND HYBRID VEHICLE PROGRAM

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ABSTRACT: The Exploratory Technology Research (ETR) Program is the electrochemical research arm of the Department of Energy Office of Transportation Technologies. The ETR Program seeks to identify new rechargeable battery and fuel-cell systems with higher performance and lower life-cycle costs than those now available, and to carry out critical supporting and materials research for batteries under development by the U.S. Advanced Battery Consortium. Lawrence Berkeley National Laboratory carries out a significant portion of the battery research. Research is also carried out at other institutions, including Lawrence Livermore National Laboratory, Brookhaven National Laboratory, Oak Ridge National Laboratory, Argonne National Laboratory, universities, and small businesses. The overall goal of the ETR Program is to develop electrochemical power sources suitable for application in electric and hybrid vehicles. The program supports research in the following areas: (*i*) rechargeable lithium batteries, (*ii*) metal-hydride/nickel oxide batteries [also known as nickel/metal-hydride], (*iii*) ultracapacitors, and (*iv*) applied science research. The ETR Program is closely coordinated with the fundamental electrochemical and materials research supported by the DOE Office of Basic Energy Sciences.

1. INTRODUCTION

The United States faces major challenges in meeting the ever growing demand for transportation goods and services, while minimizing adverse energy, environmental, and economic impacts. The transportation sector accounts for two-thirds of the U.S. oil demand. The number of vehicles on our roads and the miles driven continue to steadily increase. As a result, U. S. oil import demands continue to rise concurrently with an increase in the global demand for oil. Meanwhile, worldwide oil reserves are becoming more concentrated into a smaller number of countries. This situation leaves us increasingly vulnerable to the potentially serious adverse economic impacts of disruptions in oil supply. The large and growing levels of oil imports also represent a continuing massive transfer of wealth from the U. S. to oil exporting countries; in 1994, this was on the order of $45 billion.

There is also rising national concern about the poor air quality in U.S. cities and increasing levels of greenhouse gases. Fifty-four million Americans live in counties that regularly violate urban air quality standards. Polluting emissions from transportation sources remain a major contributor to this problem.

To address these challenges effectively, a "revolution" in transportation technologies is called for -- one which will enable us to turn the corner on growing oil imports and move toward transportation fuels that are sustainable in the long run. The Department of Energy (DOE) and other Federal programs are working to initiate and accelerate this process of "revolutionary" change. The majority of the current program resources are focused on near term, substantial increases in the efficiency with which internal combustion engines convert fuel energy into useful work. In addressing the longer term future of transportation, the widespread use of alternative fuel vehicles is essential to the program's success. Major resources are being directed to the development of alternative fuels and vehicles which will efficiently and cleanly utilize these fuels. The DOE Office of Transportation Technologies (OTT) is currently engaged in the coordination and integration of transportation technology activities involving the combined efforts of industry, national laboratories, universities, and fuel suppliers.

Within the OTT, the Office of Advanced Automotive Technologies has the primary objective to develop and validate automotive technologies which will enable the achievement of a fuel economy of 80 miles per gallon in a six-passenger sedan and be marketed domestically by 2008. This will be achieved in a manner that will comply with the ultra low emission vehicle (ULEV) standards projected to be applicable at that time. An important intermediate milestone toward achievement of this primary objective is the attainment of 50 miles per gallon in a six passenger sedan in 1998, based solely upon advances in the propulsion system. However, accomplishing 80 miles per gallon will involve simultaneous advancement and integration of multiple vehicle systems technologies.

The Office of Advanced Automotive Technologies will also pursue the development of alternative fuel vehicles that will ultimately achieve 100 miles per gallon and meet the zero emission vehicle (ZEV) standards. This technology development will consist of three paths. One path will focus on the early development of alternative fuel automobiles utilizing a variety of alternative fuels in conjunction with conventional automobile technology to achieve full range and performance capability. Another path will focus on battery development and meeting cost and performance requirements (derived with industry) to assure commercial viability of full range electric cars by 2003. Eventually, in the longer term path, efforts will be directed to advanced automobiles which will achieve 100 miles per gallon, full performance, and zero emission vehicle technologies; emphasis will be placed on the fuel cell as the primary energy conversion system. The battery programs are supported by a spectrum of exploratory research activities. This paper will focus on the results of the exploratory R&D activities during the past year.

2. EXPLORATORY TECHNOLOGY RESEARCH PROGRAM

The overall goal of the Exploratory Technology Research (ETR) Program, which is managed by Lawrence Berkeley National Laboratory (LBNL), is to develop electrochemical power sources suitable for application in electric vehicles. The program focuses on advanced systems that offer the potential for high performance and low life-cycle costs, both of which are necessary to permit significant penetration into commercial markets. This R&D Program is needed to identify advanced systems that extend battery performance beyond the current state-of-the-art and to insure that a strong technology base is available to DOE-sponsored programs, such as the U.S. Advanced Battery Consortium. The ETR Program is addressing the technical issues related to the cost, performance and operating life. The general R&D areas addressed by the program include identification of new electrochemical couples for advanced batteries, determination of technical feasibility of the new couples, improvements in battery components and materials, and establishment of engineering principles applicable to electrochemical energy storage and conversion. Major emphasis is given to applied research which will lead to superior performance and lower life-cycle costs.

Specifically, the ETR program supports research in the following areas: (i) rechargeable lithium batteries, (*ii*) metal-hydride/nickel oxide batteries [MH/NiOOH, also known as nickel/metal-hydride], (*iii*) ultracapacitors, and (*iv*) applied science research.

2.1 Batteries The U. S. Advanced Battery Consortium (USABC), a tripartite undertaking between DOE, the U.S. automobile manufacturers and the Electric Power Research Institute (EPRI), was formed in 1991 to accelerate the development of advanced batteries for EVs. Mid-term technologies under development by the USABC include lithium-ion and nickel metal-hydride batteries. Lithium/polymer batteries are being developed for the long-term.

2.1.1 Rechargeable Lithium Batteries One of the major research activities in the ETR Battery Program is to improve the performance of components for rechargeable lithium batteries that contain a polymer electrolyte, liquid electrolyte or solid-state electrolyte. Several universities are involved in research to develop polymer electrolytes with higher ionic conductivity and better chemical stability to lithium than those currently available. Theoretical analyses by molecular dynamics simulations at Northwestern University showed conclusively that in polymer/salt electrolytes of the stoichiometry usually measured, there are very few free ions, and that the conductivity is fixed both by the segmental relaxation of the polymer host and by the number of effectively free ions. These findings should be useful in tailoring the structure of polymer electrolytes to obtain improved properties for use in Li/polymer electrolyte batteries. The University of Dayton has successfully prepared three liquid crystalline monomers terminated by benzo-crown ethers using a multistep synthetic route. A procedure for preparation of films polymerized between ITO glass slides was developed and methods for aligning the liquid crystal monomers with both an electric field and a magnetic field are being explored. Alignment of the crown ethers is expected to enhance conductivity by forming a channel for lithium ions. In another approach, Case Western Reserve University has attached sulfonic acid groups to polybenzimidazole polymers to promote lithium-ion conductivity. Northwestern University has synthesized polymer electrolytes based on aluminosilicate-polyether hybrid electrolytes.

A number of efforts are aimed at the characterization of lithium battery systems. Case Western Reserve University utilized *in situ* spectroscopic techniques to study the lithium/polymer electrolyte interface, which is a major source of the problem leading to low performance and short cycle life of rechargeable Li batteries. The results with a typical polymer electrolyte composition, $PEO(LiAsF_6)$, in contact with Li suggests that under the experimental conditions selected, and to the level of sensitivity of this technique, $PEO(LiAsF_6)$ does not react with metallic Li. LANL is using nuclear magnetic resonance (NMR) spectroscopy to examine transport properties in lithium electrolyte systems.

Mathematical models provide a diagnostic tool which aid in our understanding of the physical processes taking place during operation of advanced rechargeable batteries. LBNL has developed a mathematical model of heat transport in Li/polymer batteries which revealed that the major resistance to heat transport in a Li/polymer-electrolyte battery can be attributed to the polymer electrolyte. This finding indicates that the dimensions of the Li/polymer cell stack that is used to form the battery may be limited by the heat transport properties of the polymer electrolyte.

A collaborative effort is underway between LBNL and Lawrence Livermore National Laboratory (LLNL) to identify the optimum properties of carbonaceous materials for use in electrodes to store Li for rechargeable Li/liquid electrolyte cells (Li-ion cells). Experiments are conducted at LBNL to determine the physical structure and properties of the carbonaceous materials, and LLNL tests the materials in small electrochemical cells to determine their ability to store lithium. Studies with commercially available graphite materials indicate that they are viable candidates for use in Li-ion cells. However, small-particle-size graphite (<6 microns) is needed to achieve the high discharge rates that are necessary in Li-ion batteries for EVs. Electrodes fabricated from various Superior Company graphites yielded Li intercalation capacities that range from 320 to 360 mAh/g (equivalent to x in Li_xC_6 from 0.85 to 0.95), approaching the theoretical value of 372 mAh/g corresponding to Li_xC_6. The capacity of Superior graphitized cokes is comparable to that obtained with petroleum cokes from other sources ($x \approx 0.62$) but the irreversible capacity loss is only 68 mAh/g. Analysis of a mathematical model by LBNL indicates that during normal operation, the temperature of a Li-ion battery is unlikely to reach the onset temperature for thermal runaway, however, if a battery is continuously cycled under high-rate charge and discharge, significant heat accumulation may occur.

Two novel rechargeable lithium cells, Li/S and $Li/Li_xMn_2O_4$, are being evaluated at LBNL and Oak Ridge National Laboratory, respectively. The $Li/Li_xMn_2O_4$ cell contains a solid-state electrolyte of amorphous lithium phosphorus oxynitride, and has achieved hundreds of charge/discharge cycles at low current densities (20–40 mA/cm^2), and with very little loss in performance. Efforts are underway to scale-up this technology. Research on Li/polymer electrolyte/sulfur cells was recently initiated at LBNL, and preliminary cycling tests of small cells indicate that the utilization of the sulfur electrode needs to be improved. Preliminary modeling studies indicate that smaller sulfur particles are needed to improve the sulfur utilization.

Several experimental techniques are being adapted to produce improvements in cell components for advanced rechargeable batteries. The State University of New York (Binghamton) has demonstrated that the hydrothermal method provides a route to synthesize metal oxides at lower temperatures than those conventionally used. Molybdenum oxides (MoO_3) for positive electrodes in rechargeable Li cells prepared by this method exhibited a higher capacity than the normal MoO_3 phase. Covalent Associates have synthesized Cr-doped $LiMn_2O_4$ (7 mol% Cr), which showed stable charge/discharge cycling but the performance was lower than that obtained with the spinel $LiMn_2O_4$.

2.1.2 Nickel/Metal-Hydride Batteries The ETR Program supports the development of low-cost metal hydride electrodes for nickel-metal hydride cells. X-ray absorption spectroscopy (XAS) studies of AB_2 alloy hydrides by Brookhaven National Laboratory (BNL) indicated the presence of strong interactions between the interstitial H atom and Ti, V and Zr. Very little interaction between H and Ni was observed, suggesting that the role of Ni in the AB_2 alloys is primarily catalytic in nature. BNL has observed that the co-precipitation of Co^{2+} ions into the $Ni/Ni(OH)_2$ electrode reduced the drop in charge efficiency to ~25% after long-term cycling, compared to ~50% drop in electrodes without Co. They also studied nickel oxide electrodes in aqueous alkali electrolytes after charge/discharge cycling and found that corrosion may be a life-threatening problem with certain types of electrode construction. The University of South Carolina is conducting research to improve the performance of metal hydride electrodes. Experimental hydrogen storage capacities of bare and Cu-coated LaNiSn alloy were found to be 270 and 275 mAh/g, respectively, about 76 and 78% of the theoretical capacity. The University of Michigan is modeling the performance of MH/NiOOH batteries. Materials have been characterized microscopically, and simulations have been initiated to characterize transport in model microstructures.

2.2 Ultracapacitors Ultracapacitors are an enabling technology that, when combined with batteries, can yield a high-performance electrical energy storage system for EVs. They also have the potential to satisfy the electrical energy storage requirements of hybrid and fuel cell vehicles. Present R&D is focused on increasing the specific energy of ultracapacitors. Both carbon-based and metal oxide systems are being explored. SAFT Research & Development Center is evaluating activated carbons in electrochemical double-layer capacitors, and conducting a systematic study of various electrode binders. The University of Wisconsin is investigating metal oxides for double-layer capacitors. They have observed that the specific capacitance of NiO/Ni electrodes in 1 M LiOH is as high as 120 F/g of active material. A model of electrochemical double layer capacitors during operating conditions has been developed at LBNL which indicates that side reactions during overcharge and overdischarge which may involve decomposition of the electrolyte have a pronounced impact on the cycling behavior.

2.3 Applied Science Research The objectives of the applied science research are to provide and establish scientific and engineering principles to batteries and electrochemical systems; and to identify, characterize and improve materials and components for use in batteries and electrochemical systems. The projects provide research that supports a range of battery systems that contain solid electrolyte and nonaqueous electrolytes that are both liquid, gel and polymer. The cross-cutting research efforts are directed at improving the understanding of electrochemical engineering principles, minimizing corrosion of battery components, analyzing the surface of electrodes and using the results to increase energy density, power and life.

Electrode characterization studies are an important research element for the successful development of rechargeable electrodes for advanced secondary batteries. Efforts are underway to evaluate the performance of cells utilizing Li intercalation electrodes, and use advanced spectroscopic techniques to investigate the chemical state of electrode materials during charge/discharge cycling. Components for ambient-temperature nonaqueous cells, particularly metal/electrolyte combinations that improves the recharge ability of these cells, are under investigation. Research is carried out to develop mathematical models of electrochemical systems and to address fundamental problems in current-density distribution; solutions will lead to improved electrodes structures and performance in batteries.

2.3.1 Posters illustrating Exploratory Technology research at this conference include :

Advanced Battery Research At Lawrence Berkeley National Laboratory
K. Kinoshita, Lawrence Berkeley Laboratory

Battery Materials: Structure and Characterization
J. Mcbreen, Brookhaven National Laboratory

Applied Research on Novel Cell Components for Advanced Secondary Batteries and Capacitors
A.-M. Sastry, University of Michigan

3. CONCLUSION

The Exploratory Technology Research Program continues to make significant contributions to the development of advanced battery systems. ETR activities are closely coordinated with other DOE efforts involving these technologies, and with the fundamental research activities supported thorough the DOE Office of Basic Energy Sciences. All R&D activities are also coordinated with programs supported by other U.S. government agencies. Finally, international cooperation is achieved through our participation in the International Energy Agency.

REFERENCES

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